Optical Materials 36 (2014) 1515–1519

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Rare-earth antisites in lutetium aluminum garnets: Influence on lattice parameter and Ce^{3+} multicenter structure

H. Przybylińska [a], A. Wittlin [a,b], Chong-Geng Ma [c], M.G. Brik [d], A. Kamińska [a], P. Sybilski [a], Yu. Zorenko [e], M. Nikl [f], V. Gorbenko [e,g], A. Fedorov [h], M. Kučera [i], A. Suchocki [a,e,*]

[a] Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
[b] Cardinal Stefan Wyszyński University in Warsaw, ul. Dewajtis 5, 01-815 Warsaw, Poland
[c] College of Mathematics and Physics, Chongqing University of Posts and Telecommunications, Chongqing 400065, PR China
[d] Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia
[e] Institute of Physics, Kazimierz Wielki University, Weyssenhoffa 11, 85-072 Bydgoszcz, Poland
[f] Institute of Physics AS CR, Cukrovarnicka 10, 16253 Prague, Czech Republic
[g] Department of Electronics Ivan Franko National University of Lviv, 107 General Tarnavskyj Str., 79017 Lviv, Ukraine
[h] Institute for Scintillation Materials of NAS of Ukraine (ISMA), Lenin avenue, 60, Kharkov 61158, Ukraine
[i] Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, 12116 Prague 2, Czech Republic

ARTICLE INFO

Article history:
Received 28 December 2013
Received in revised form 6 April 2014
Accepted 15 April 2014
Available online 5 May 2014

Keywords:
Garnets
Scintillators
Laser materials
Phosphors

ABSTRACT

Low temperature, infrared transmission spectra of lutetium aluminum garnet (LuAG) bulk crystals and epitaxial layers doped with Ce are presented. In the region of intra-configurational *4f–4f* transitions the spectra of the bulk LuAG crystal exhibit the signatures of several different Ce^{3+} related centers. Apart from the dominant center, associated with Ce substituting lutetium, at least six other centers are found, some of them attributed to so-called antisite locations of rare-earth ions in the garnet host, *i.e.*, ions in the Al positions. X-ray diffraction data prove lattice expansion of bulk LuAG crystals due presence of rare-earth antisites.

1. Introduction

Lutetium aluminum garnets, with the chemical formula $Lu_3Al_5O_{12}$ (LuAG), doped with Ce both in the form of single crystals and epitaxially grown layers belong to the class of most successfully applied scintillators [1,2], due to the high density of the matrix. They are also subject of numerous studies as candidates for solid state laser materials [3,4], and phosphors.[5–10] Ce^{3+} ions in LuAG form very efficient luminescence centers, originating from parity allowed inter-configurational $4f^05d^1 \rightarrow 4f^15d^0$ transitions, with the relatively simple $4f^15d^0$ ground state configuration. Trivalent rare-earths ions either as constituents of the host or as dopants are usually located in dodecahedral sites in the garnet structure. However, in Czochralski grown bulk crystals the so-called antisites are also found, *i.e.*, rare-earth ions replacing aluminum in sites with octahedral symmetry [11]. The idea of antisite formation in garnets first was proposed on a basis of differences in lattice parameters of Czochralski grown crystals and powders prepared by solid state reaction [12–14]. Later on, the problem of antisite defect formation in garnets was discussed thoroughly in Refs. [15–17], and [18], along with proposed models of such defects. In addition, other types of rare-earth and transition metal centers occur often in garnets [19,20]. In contrast, epitaxially grown garnet layers contain much less antisites of rare-earth ions [21,20]. This is due to the significantly lower (in the 950–1050 °C range) growth temperature of the epitaxial layers in comparison with their bulk counterpart (around 2000 °C). This is of importance, since antisite defects influence immensely the optical properties of scintillator materials, having sometimes detrimental effects on their characteristics, as, for example, slowing-down the scintillation response and decreasing the light yield. One of the methods used to improve the scintillation properties of LuAG crystals is either to avoid the formation of Ce multicenters by the use of low temperature grown epitaxial layers or by quenching their luminescence with use of band-gap engineering. The knowledge about the energy structure of the Ce multicenters and their nature in LuAG crystals and epitaxial layers may greatly help to improve the properties of LuAG as scintillator material and lead to its further development.

* Corresponding author at: Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland. Tel.: +48 228436861.
E-mail address: suchy@ifpan.edu.pl (A. Suchocki).

http://dx.doi.org/10.1016/j.optmat.2014.04.015
0925-3467/

Although LuAG:Ce is very important from the point of view of applications, up to now there is little information on the Ce multicenter structure in this material. It is known that certain antisite-type defects are formed there [22]. The confirmation of the existence of Ce^{3+} antisite centers was proven in Ref. [20] with use of EPR spectroscopy. In the latter work, apart from Ce^{3+}_{Lu} ions in regular Lu positions, the Ce^{3+}_{Al} antisite centers and two other types of Ce^{3+}_{Lu} centers strongly interacting with LuAl antisite defects were found as well [20].

This work is devoted to low temperature far-infrared transmission studies of LuAG:Ce single crystals and epitaxial layers with the aim to study the origin of Ce multicenters The results are supported by X-ray diffraction (XRD), which confirm the RE-antisite presence in this material. Recently, we demonstrated such spectroscopic evidences for gadolinium gallium garnet bulk crystals [23], and also yttrium aluminum garnet bulk crystals and epitaxial layers [24].

2. Samples and experimental procedures

The LuAG:Ce bulk crystal used in our study, obtained from CRYTUR Company, was grown by the Czochralski method in a molybdenum crucible with use of 5 N raw materials. The Ce content in the crystal was about 0.09 at.%. LuAG:Ce single crystalline films (SCF) were grown by liquid phase epitaxy (LPE) in a platinum crucible from the melt solution, containing the $PbO–B_2O_3$ flux and Lu_2O_3, CeO_2 and Al_2O_3 crystal-forming oxides of 5 N purity, on both sides of (1 1 0) oriented LuAG substrates [25,26]. For transmission studies samples with total thickness of around 127 μm were selected. The average Ce content in the layers was equal to about 0.2 at.%. The infrared absorption spectra were measured with a VERTEX 80v (Bruker) and a BOMEM DA3 Fourier-Transform Infrared (FTIR) spectrometers, with resolution of 1 cm^{-1}. For low temperature measurements the samples were placed into a cold finger of Oxford Instruments CF-102 continuous-flow cryostat equipped with KBr windows.

The XRD investigations were applied for estimation of the structural disorder in LuAG single crystals, grown by the Czochralski method at a temperature of 2010 °C, and LuAG single crystalline layers, grown by the LPE method in the 1030–1050 °C temperature range from melt-solution based on the $PbO–B_2O_3$ flux onto LuAG substrates with (1 1 1) orientation. Due to low growth rate (0.15–0.25 μm/min) and relatively high temperature range of LuAG SCF growth, we kept the concentration of Pb^{2+} related dopant in these SCF below 30 ppm. XRD measurements were performed using the DRON-4 double crystal spectrometer with Si (4 0 0) monochromator (Cu Kα radiation).

3. Experimental results and discussion

The energy structure of Ce^{3+} ions with $4f^1$ configuration consists of a $^2F_{5/2}$ ground state and a $^2F_{7/2}$ excited state, which arise from the ^2F term due to spin-orbit interaction. The crystal field (CF) splits these two states further into three (levels #1–3) and four (levels #4–7) energy levels, respectively.

The absorption spectrum of the LuAG:Ce(0.09 at.%) bulk sample taken at 5 K in the region of the *4f–4f* transitions is presented in Fig. 1. A spurious background was subtracted from the spectra. The four groups of lines in Fig. 1 are attributed to optical transitions between the lowest-lying level (#1) of the ground $^2F_{5/2}$ state and four levels of the $^2F_{7/2}$ excited state of Ce^{3+}. Each group consists of several lines, which means that several Ce^{3+} – related center contribute to the spectrum. The lines around 2360 cm^{-1}, associated with transitions between levels #1 and #6 are partially overlapped, therefore the lines associated with various Ce^{3+} centers are not resolved for these transitions. The lines close to 3000 cm^{-1} are associated with the hydroxyl group vibrations.

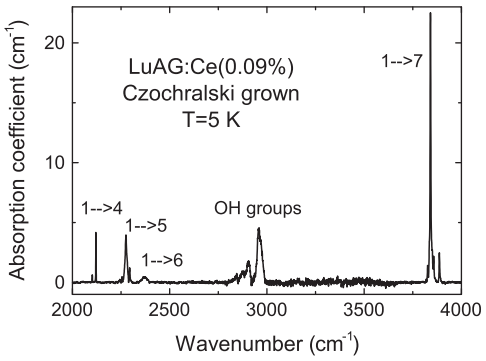

Fig. 1. Absorption spectrum of the bulk LuAG:Ce (0.09 at.%) sample taken at 5 K in the region of Ce^{3+} *4f–4f* transitions. Transitions designations are marked on the graph.

Evident multicenter structure of Ce^{3+} dopant in LuAG can be the more easily observed in the region of the strongest absorption associated with the transitions from the levels #1 to levels #7 of various Ce^{3+}-related centers, presented in Fig. 2.

In addition to the major line with a peak at 3841 cm^{-1}, which we associate with the Ce^{3+} ions in regular Lu dodecahedral positions, at least six other lines are visible on both sides of this line. The three strongest lines occur at 3826, 3858, and 3889 cm^{-1}, the remaining ones are located at the wings of the dominating 3841 cm^{-1} line. The total intensity ratio of these three lines to the ones grouped around 3841 cm^{-1} is about 20%, which is a relatively large value. Full width at half of the maximum of the particular lines in the spectrum is between 4 and 6 cm^{-1}.

At an elevated temperature of 105 K, there are additional lines in the transmission spectrum of the LuAG:Ce Czochralski grown crystal. These lines are associated with the population of the second levels of the $^2F_{5/2}$ state and transitions from these levels to the different levels of the various Ce^{3+} centers. Fig. 3 shows these additional lines in the region of transitions terminating at level #7.

Two partially overlapped lines can be distinguished around 3620 cm^{-1}. Assuming that the stronger of these lines, peaked at 3618 cm^{-1}, is associated with the major Ce^{3+} center, and the weaker one with a peak at 3631 cm^{-1}, associated with the second most abundant Ce^{3+} center, we obtain the separation between the two lowest levels of the ground $^2F_{5/2}$ state as equal to 223 cm^{-1} for the major Ce^{3+} center and 254 cm^{-1} for the second most abundant Ce^{3+} center in LuAG.

The low temperature absorption spectrum of the LuAG epitaxial layer is presented in Fig. 4. Three major lines associated with Ce^{3+} absorption are observed, related to optical transitions between level #1 and levels #4, #5, and #7. Comparison of this spectrum with that measured in the LuAG bulk crystal in the region of #1 → #7 transitions (see Fig. 2) shows that though the additional lines around the major peak are still easily discernible their intensities, with reference to the major line at 3841 cm^{-1}, are much lower in the epitaxial layer than in the bulk crystal. This confirms that epitaxial grown layers contain much less Ce^{3+} multicenters, in particular the Ce antisites (Ce^{3+}_{Al}). Dominating lines associated with Ce^{3+} on Lu sites (Ce^{3+}_{Lu}) are visible, except of the low intensity line associated with transition between levels #1 and #6. The FWHM of the lines associated with transitions between levels #1 and #7 are similar in the epitaxial layer and in the bulk crystal.

A large number of Ce^{3+} multisites is observed in examined crystals, with quite abundant concentrations as compared to the concentration of the major Ce^{3+} – related center. That observation remains valid, even taking into account that the absorption